

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number
WO 01/14601 A1

(51) International Patent Classification?: **C21D 6/02, B26B 19/02, 19/14**

(21) International Application Number: **PCT/SE00/01634**

(22) International Filing Date: 23 August 2000 (23.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9902977-9 23 August 1999 (23.08.1999) SE

(71) Applicants: **SANDVIK AB; (publ) [SE/SE]; S-811 81 Sandviken (SE). KONINKLIJKE PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).**

(72) Inventors: **NILSSON, Jan-Olof; N Hasselgatan 11, S-811 35 Sandviken (SE). OLSSON, Sören; Kalvdansvägen 33 C, S-811 38 Sandviken (SE). SJOERD BLAAUW,**

Hubert; Voergang 33, NL-9205 AV Drachten (NL). VAN DER GRIJN, Adriaan; Mariengaard 58, NL-9202 GC Drachten (NL).

(74) Agent: **TÅQUIST, Lennart; Sandvik AB, Patent Dept., S-811 81 Sandviken (SE).**

(81) Designated States (national): **CN, JP, KR.**

(84) Designated States (regional): **European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).**

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



A1

WO 01/14601 A1

(54) Title: **METHOD FOR THE MANUFACTURE OF STEEL PRODUCTS OF A PRECIPITATION HARDENED MARTENSITIC STEEL, STEEL PRODUCTS OBTAINED WITH SUCH METHOD AND USE OF SAID STEEL PRODUCTS**

(57) Abstract: A method for the manufacture of steel products and products thus produced, wherein steel is subjected to isothermal martensitic formation and precipitation hardening in a martensitic structure subsequent to soft annealing and shaping. The method steps include shaping followed by solution annealing between 1050 °C and 1200 °C, quenching from the solution annealing temperature with a quenching speed of at least 5 °C per second to a temperature below 500 °C, subjecting said steel to an isothermal martensitic transformation and subsequently hardening the steel at a temperature between 450 °C and 550 °C to precipitate particles in said martensitic structure.

-1-

**METHOD FOR THE MANUFACTURE OF STEEL PRODUCTS OF A
PRECIPITATION HARDENED MARTENSITIC STEEL, STEEL
PRODUCTS OBTAINED WITH SUCH METHOD AND USE OF SAID
STEEL PRODUCTS**

FIELD OF THE INVENTION

The present invention relates to a method for the manufacture of a steel product wherein the steel is subjected to isothermal martensite formation and precipitation hardening in a martensitic structure subsequent to soft annealing and is shaping. The invention also relates to a steel product obtained with such method and to the use of said steel product.

BACKGROUND OF THE INVENTION

In the discussion of the state of the art that follows, reference is made to certain structures and/or methods. However, the following references should not necessarily be construed as an admission that these structures and/or methods constitute prior art. Applicant explicitly reserves the right to demonstrate that such structures and/or methods do not qualify as prior art against the present invention.

In published international patent application WO93/07303, a method of manufacture of the above mentioned kind has been described wherein the transformation into the martensitic structure is accomplished by air cooling after annealing in the austenitic region or by cold working. Air cooling after annealing normally results in the so-called athermal kinetic mode of martensite transformation. The formation of air cooling induced martensite is suppressed by alloying elements like nickel, titanium and aluminum, which are used for precipitation of hardenable steel. It may be that at relatively high concentrations of such alloying elements the austenite is stabilized

-2-

such that the martensitic transformation start temperature becomes impractically low.

SUMMARY OF THE INVENTION

It is an object of the invention to offer a method for the manufacture of steel products, steel products so manufactured and the use of said steel products whereby a practical optimum is achieved between ductility, strength, wear and corrosion resistance, homogeneity of martensite distribution and a practical level of the martensite transformation temperature.

One aspect of the present invention is a method for the manufacture of a steel product comprising the steps of subjecting the steel to isothermal martensite formation and precipitation hardening in a martensitic structure subsequent to soft annealing. The steel is then shaped into the desired form subsequent to soft annealing, followed by solution annealing at a temperature between 1050°C and 1200°C and for a time period of between 5 and 30 minutes. From the annealing temperature, the steel is quenched at a rate of at least 5°C per second to a temperature below 500°C. The quenched steel being subjected to an isothermal martensitic transformation. Precipitation hardening of the steel is then accomplished at a temperature of between 450°C and 550°C for at least 3 minutes to cause precipitation of particles in the martensitic structure.

BRIEF DESCRIPTION OF THE DRAWING FIGURE

The objects and advantages of the invention will become apparent from the following detailed description of preferred embodiments thereof in connection with the accompanying drawing.

-3-

Figure 1 is a temperature profile in time of the heat treatment and processing method of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A method for the manufacture of a steel product according to the invention is characterized by shaping of the steel followed by solution annealing between 1050°C and 1200°C for between 5 and 30 minutes, after which the steel is quenched from the solution annealing temperature to a temperature below 500°C with a quenching speed of at least 5°C per second. The quenched steel is then subjected to an isothermal martensitic transformation and is subsequently strengthened by being held at a temperature between 450°C and 550°C for at least 3 minutes to precipitate particles in the martensitic structure.

A combination of an isothermal martensitic transformation and precipitation hardening is known (See Scripta Metallurgica et Materialia, 1995, Vol. 33, No. 9, pp. 1367-1373). However, a method of manufacture of the above-mentioned kind which allows a steel product to be formed into a relatively complicated shape by deformation whilst achieving an optimum between ductility, strength, wear and corrosion resistance and homogeneity of martensite distribution is not disclosed. It is a further object of the invention to provide a very efficient method for the manufacture of steel products with a homogeneous distribution of martensite and precipitates.

Accordingly, a method for the manufacture of steel products according to the invention is further characterized by subjecting the quenched steel to an isothermal martensitic transformation by holding the steel at a temperature between -30°C and -50°C for at least one hour.

-4-

A method for the manufacture of steel products according to the invention is still further characterized by a sensitizing procedure in which the steel is held at a temperature between 850°C and 950°C for at least 5 minutes so as to allow initiation of the martensitic transformation to become optimal. The sensitizing procedure occurs between solution annealing and quenching the steel. A steel subjected to a sensitizing procedure alleviates thermo-mechanical stresses which would otherwise build up internally in the steel product. The reduced internal thermo-mechanical stresses enable the manufacture of a steel product with a very accurate size and which is stable in use.

A further object of the invention is to provide a method of manufacture of a steel product exhibiting a combination of superior strength, corrosion resistance and ductility. Such a method is further characterized in that the steel comprises chromium (Cr) in a weight percentage between 10 % and 14 %. Generally, martensitic steels with a low weight percentage of carbon, so-called maraging steels, may be with or without chromium. Corrosion resistant maraging steels comprise a weight percentage of chromium between 10.5 and 18 %. A particular type of maraging steel, which may be obtained by the method according to the invention, contains in weight percentage 10-14 % Cr, 7-10 % Ni, 3-6 % Mo, 0-9 % Co, 0.5-4 % Cu, 0.05-0.5 % Al, 0.4-1.4 % Ti and less than 0.03 % C and N.

The invention will be elucidated further by the use of practical examples:

Example 1

A steel material suitable for use with the present invention with the above mentioned composition was produced as a strip material from a full scale seven ton melt in a high frequency furnace and then subjected to rolling. The solidification process after melting 1 is shown in figure 1 in which the temperature profile over time is indicated by a solid line. Solidification of the melt leads to crystallization of Ti (C,

-5-

N), thereby binding the free carbon and free nitrogen. The binding of free nitrogen is important because the free nitrogen would otherwise suppress the isothermal martensitic transformation.

Before rolling, the steel is reheated to a temperature of 1150°C to 1250°C and soaked at this temperature for at least 1 hour in order to give the material an austenitic structure and sufficient ductility to be hot rolled. Reheating to a temperature of 1150°C to 1250°C 2 is followed by hot rolling 3. Hot rolling 3 produces a material in a strip shape with a suitable grain size and evenly distributed intermetallic particles.

Scale (oxide layers) formed during soaking and hot rolling has to be removed by pickling and/or grinding before the material can be cold rolled to final dimensions. Cold rolling 4 gives the strip steel the final thickness without formation of oxide layers. Cold rolling 4, however, leads to strain induced martensitic transformations and, to ensure sufficient ductility to form a complicated product, the material has to be brought back into the austenitic condition by annealing 5. This annealing 5 is carried out in a continuous furnace at a temperature around 1050°C, to prevent the material from transforming to martensite before shaping of the product. The product is cold formed in the austenitic condition 6 leading to a partial transformation to strain induced martensite. To ensure a homogeneous martensite transformation throughout the product and sufficient hardenability of the formed martensite by precipitation hardening, the material has to be solution annealed 7 for 5 to 30 minutes at a temperature between 1050°C and 1200°C. Solution annealing 7 also causes alloying elements, such as Al, Cu, Mo and Ti to go into solution in the austenitic structure and reversion of strain induced martensite to austenite. These elements are used for precipitation hardening of the isothermal martensite at a later stage of the manufacture.

-6-

In order to achieve an optimal isothermal martensitic transformation 10, the martensitic transformation 10 should be carried out at a temperature between -30°C and -50°C for at least one hour. More preferably, the isothermal martensitic transformation 10 is preceded by a sensitizing process 8. The sensitizing process 8 is positioned between a solution annealing step 7 and a quenching step 9. The sensitizing process 8 occurs when the steel is held at a temperature between 850°C and 950°C for at least five minutes. The sensitizing process 8 causes destabilization of the austenitic structure of the steel material and so facilitates the subsequent isothermal martensitic transformation 10. It has been determined that during the sensitizing process 8, Mo and Ti are removed from the solution and it is believed that Mo concentrates along crystal boundaries. The behavior of Ti is not yet clear. Sensitization further ensures homogeneous nucleation of martensite during the isothermal martensitic transformation 10. Quenching 9 to room temperature or even lower prevents premature precipitation of essential intermetallic compounds in the austenite.

After quenching 9, the steel material is subjected to an isothermal martensitic transformation 10. This transformation is accomplished by holding the steel at a temperature of -30°C to -50°C for at least one hour. The result is a homogeneous martensitic structure with uniformly distributed retained austenite in a fine grain size. The isothermal martensitic transformation 10 is followed by a hardening procedure 11 during which intermetallic compounds precipitate solution in the martensitic structure. The steel product so treated will have a homogeneous hardness of more than 450 HV.

A steel product which is obtained by the present method is homogenous and exhibits excellent properties with respect to wear, corrosion resistance, hardness and ductility. This unique combination of properties makes the strip steel product very attractive for shaver caps of electric rotary shavers, which are subjected to deep

-7-

drawing during manufacture in order to obtain the necessary bowl shape. The same applies to the heavily deformed cutters of shavers, the strongly shaped knives of blenders and the strongly folded return springs for thermostats in irons.

The chemical composition in weight percentages of a steel material, which is very well suited to be subjected to the treatment method according to the present invention is as follows (so-called Sandvik 1RK91 steel):

C+N	≤ 0.05
Cr	12.00
Mn	0.30
Fe	balance
Ni	9.00
Mo	4.00
Ti	0.90
Al	0.30
Si	0.15
Cu	2.00

Example 2

A steel material or product with the same chemical composition as in Example 1 may be produced as a diaphragm plate spring functioning as a return spring in a fluid valve. Depending on the required accuracy of the diaphragm plate spring dimensions, it may be allowed to have so-called retained austenite in the product after quenching 9. Solution treatment 7 is preferred followed by sensitizing 8 which causes destabilization of the austenite so that the later isothermal martensitic transformation 10 is facilitated. Diaphragm plate springs for many applications use complicated shapes which require strong deformations during forming. Such

-8-

deformations cause strain induced martensite which has to be reversed into austenite by solution treatment 7. The method of the present invention is well suited to preparing the steel stock for this application.

Although the present invention has been described in connection with preferred embodiments thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without departing from the spirit and scope of the invention as defined in the appended claims.

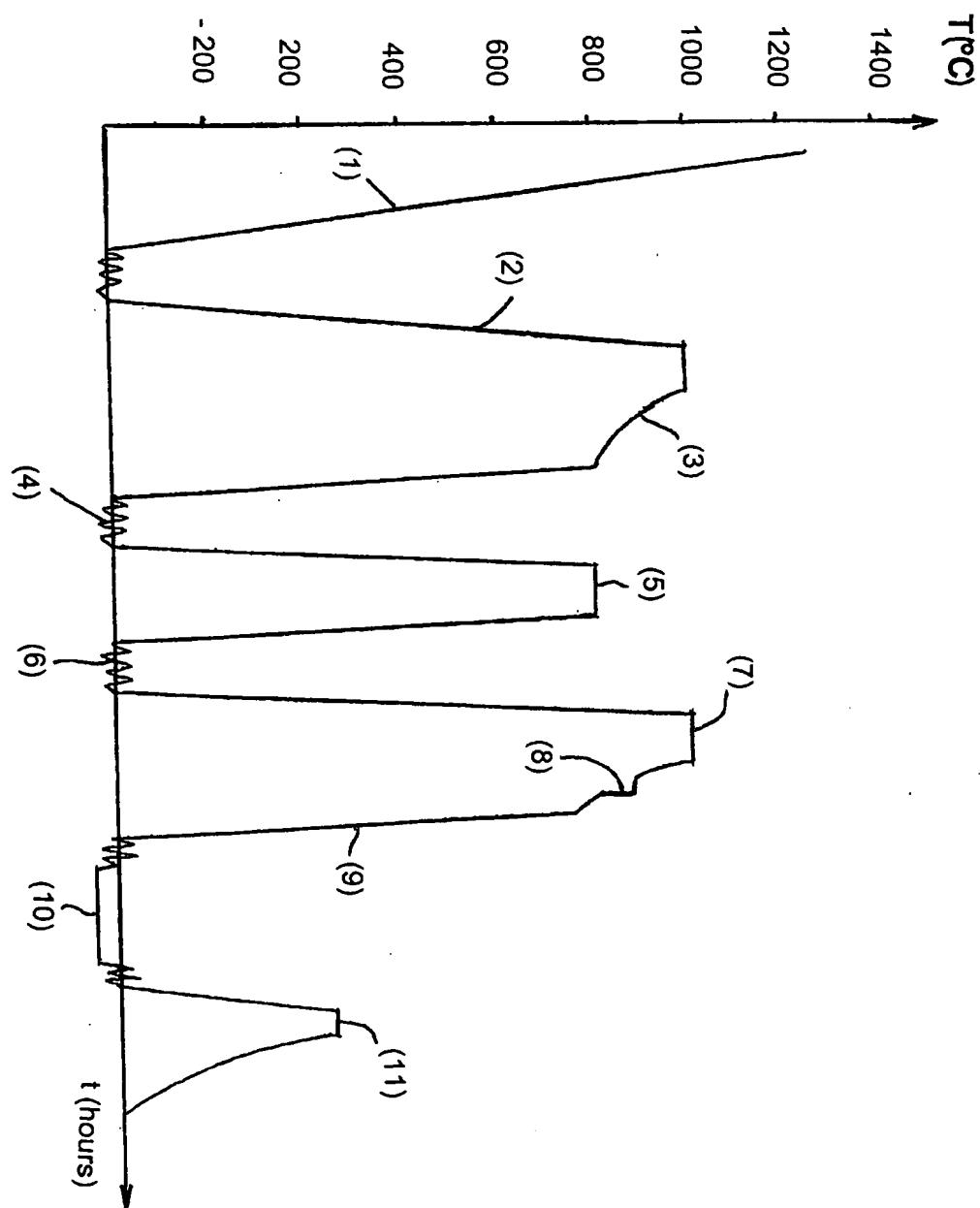
CLAIMS

1. A method for the manufacture of a steel product comprising the steps of:
 - (a) subjecting the steel to precipitation hardening in a martensitic structure subsequent to soft annealing;
 - (b) shaping said steel, followed by solution annealing between a temperature of 1050°C and 1200°C and for a time period of between 5 and 30 minutes;
 - (c) quenching the steel from the solution annealing temperature to a temperature below 500°C with a quenching rate of at least 5°C per second, said quenched steel being subjected to an isothermal martensitic transformation; and
 - (d) hardening at a temperature between 450°C and 550°C for at least 3 minutes to cause particles to precipitate out from solution into the martensitic structure.
2. The method according to claim 1, wherein the quenched steel is subjected to an isothermal martensitic transformation at a temperature between -30°C and -50°C for at least one hour.
3. The method according to claim 1, wherein, between the solution annealing and the quenching of the steel, the steel is subjected to a sensitizing procedure between 850°C and 950°C for at least 5 minutes thereby optimizing initiation of the isothermal martensitic transformation.
4. The method according to claim 3, wherein the sensitizing procedure homogeneously nucleates martensite during the isothermal martensitic transformation.

-10-

5. The method according to claim 1, wherein the steel comprises chromium (Cr) in a weight percentage between 10 % and 14 %.
6. A steel product manufactured by the method of claim 1 having a homogenous hardness of at least 450 HV.
7. The steel product of claim 6, wherein the steel product is a cap of an electric rotary shaver.
8. The steel product of claim 6, wherein the steel product is a cutter of an electric rotary shaver.
9. The steel product of claim 6, wherein the steel product is a cutter in a domestic appliance.
10. The steel product of claim 6, wherein the steel product is a knife in a domestic appliance.
11. The steel product of claim 6, wherein the steel product is a spring in a domestic appliance.
12. The steel product of claim 6, wherein the steel product is a medical instrument.
13. The steel product of claim 6, wherein the steel product is a dental instrument.
14. The steel product of claim 6, wherein the steel product is a diaphragm plate spring in a fluid valve.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 00/01634

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C21D 6/02, B26B 19/02, B26B 19/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C21D, B26B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Scripta Metallurgica et Materialia, Volume 33, No 9, 1995, M. Holmquist et al, "Isothermal Formation of Martensite In A 12Cr-9Ni-4Mo Maraging Stainless Steel" page 1367 - page 1373	1-6
A	-----	7-14

 Further documents are listed in the continuation of Box C. See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 December 2000	20-12-2000
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer Anna-Maj Magnusson/E1s Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE00/01634

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see next page

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE00/01634

The search showed that both the method according to claim 1 and the product according to claim 6 are known. Consequently, a posteriori, claims 7-14 do not fulfil the requirement of unity of invention and define a total of 8 different inventions, namely:

- I: a cap of an electric rotary shaver according to claim 7
- II: a cutter of an electric rotary shaver according to claim 8
- III: a cutter in a domestic appliance according to claim 9
- IV: a knife in a domestic appliance according to claim 10
- V: a spring in a domestic appliance according to claim 11
- VI: a medical instrument according to claim 12
- VII: a dental instrument according to claim 13
- VIII: a diaphragm plate spring in a fluid valve according to claim 14

It might also be mentioned already here that claims 7-14 also lack clarity in the way that they refer to the steel product in claim 6, which is manufactured by the method in claim 1. As the method of claim 1 could not result in any of the products in claims 7-14, e.g. a cap of an electric rotary shaver in claim 7, claims 7-14 are inconsistent and unclear, cf. PCT Examination Guidelines chapter III, paragraph 4.4.